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**PHASE DIAGRAM MODELLING:
NICKEL - ALUMINUM - CHROMIUM
SYSTEM**

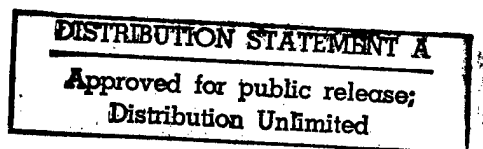
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Phase Diagram Modelling:
Nickel - Aluminum - Chromium System

Captain Kevin M. Jaansalu
Air Vehicle Research Detachment

The Ni-Al-Cr system is of importance to the gas turbine industry as it forms the basis for protective coating design and application for hot section components. These thermodynamic models establish a foundation upon which the metallurgical chemistry of aluminum coating processes for nickel base superalloys can be addressed. The thermodynamic model of the ternary system is based on the binary phase diagrams for each pair of components. Given the technological importance of this system, the robustness of the models developed for each of the binary systems will have a direct impact on the success of future engineering work. It is primarily for this reason that these binary systems are examined in detail. This technical memo reviews the thermodynamic concepts upon which phase diagram models are based and presents an effective model for each of the binary systems: Al-Cr, Al-Ni, and Ni-Cr.

Phase Diagram Modelling

Nickel - Aluminum - Chromium System

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Introduction

The Ni-Al-Cr system is of importance to the aero gas turbine industry as it forms a basis for protective coating design and application for hot section components. The nickel based superalloys are designed and/or treated so that a protective layer of aluminum oxide is formed in service. If there is damage to this protective layer, the scale will re-generate. This requires metallurgical conditions such that the formation of aluminum oxide is thermodynamically and kinetically favoured. It is a common industrial practice to surface treat nickel based components so that the alumina scale will form and that there is a sufficient reservoir of aluminum to re-generate the scale throughout the service life of the component. Common treatments include thermal sprayed metal-chromium-aluminum-yttrium coatings (MCrAlY), and pack cementation processes for forming an aluminum rich surface layer on the component. This work was initiated to establish a foundation upon which the metallurgical chemistry of aluminum coating processes could be addressed.

The foundation of the ternary system consists of the binary phase diagrams for each pair of components. Each binary will be modelled and the resulting treatments can then be used to derive the ternary diagram using various mathematical approaches. The various thermodynamic calculations required for phase diagram modelling will be undertaken with the use of the "Facility for the Analysis of Chemical Thermodynamics" (FACT), a computer software package consisting of programs and an extensive compound database. Given the technological importance of the Ni-Al-Cr system, the robustness of the models developed for each of the binary systems will have a direct impact on the success of future engineering work. It is primarily for this reason that these binary systems are examined in detail. This paper will review the thermodynamic concepts which result in phase diagram models and present a model for each of the binary systems.

Thermodynamic Equations

The calculation of metal alloy phase diagrams makes constant use of the concept of partial molar properties. In general, for any extensive property M , the partial molar quantity due to the i^{th} component, \bar{M}_i , can be defined at constant temperature, pressure, and number of moles of all other components j , as:

$$\overline{M}_i = \left(\frac{\partial M}{\partial n_i} \right)_{T,P,n_j} \quad (1)$$

The partial molar property \overline{M}_i may be regarded as the contribution per mole of element in the solution. For the calculation of phase diagrams at constant pressure, the partial molar Gibbs energy is used. But first, as the Gibbs energy is an extensive property, it may be re-written as an energy per mole:

$$G = G(n_1 + n_2 + \dots + n_i + \dots) \quad (2)$$

where G is the extensive Gibbs energy, G is the Gibbs energy per mole of solution, and n_i is the number of moles of component i . Substituting (2) for the extensive molar property in (1) above and converting from number of moles to mole fraction x for a binary system, the resulting equation is:

$$\overline{G}_1 = G + x_2 \left(\frac{\partial G}{\partial x_1} \right)_{P,T} \quad (3)$$

Equation 3 then gives the partial molar Gibbs energy as the intercept at $x_1=0$ of the line tangent to the curve representing G , as illustrated at Figure 1 below. Similarly, the same line extended to the right to $x_1=1$ will give the partial molar energy for component 2.

When the Gibbs energy of the system under consideration is at a minimum, the system is at equilibrium. For a binary system at constant temperature, equilibrium between two phases occurs when the partial molar properties of component i are equal in both phases. In Figure 1, at 1700 K and at $x_{Ni} = 0.25$, the stable phase is liquid as the tangent drawn at this point does not cross any other energy curve. The Gibbs energy is at a minimum. However, as the mole fraction of nickel increases, the slope of the tangent will slowly become more positive (rotate counter clockwise). There will be a point where the tangent to the liquid curve will also be tangent to the bcc curve, as shown in Figure 2. From equation 3 above, the endpoints of this tangent give the partial molar energy of the element in a particular phase and when the tangent is common to two curves, the partial molar energy of aluminum in the two phases are the same, as well the partial molar energies for the nickel in the two phases will be the same. On a phase diagram, this tangent corresponds to the liquidus- solidus tie line at 1700 K. The liquidus composition and solidus composition are depicted by points A and B respectively. As the mole fraction Ni increases further, note that although the energy curves intersect at composition C, a mixture of the two phases of compositions represented by A and B will have the lowest Gibbs energy. This demonstrates the concept that the equilibrium compositions are represented by the lowest common tangent which can be derived as a consequence of equation 3 and that the Gibbs energy must be at a minimum.

In computing these energy curves, it must be kept in mind that the Gibbs energy cannot be calculated as an absolute number, but must always be relative. Indeed, it is these relative differences that are important and it is critical that these differences are kept clear in the formulation of the equations that lead to the Gibbs energy curves.

In metallurgical phase diagram calculations, it is common practice to select the liquid phase of both pure metals as the reference phases, and their Gibbs energy is arbitrarily defined to be zero at all temperatures and pressures. This can be seen in Figures 1 and 2 where the liquid energy curve is at zero for both pure components. The energy curve for the fcc phase is positive with respect to liquid at pure aluminum (aluminum at 1700 K is molten) and the fcc curve is negative with respect to liquid at pure nickel (nickel melts at 1728 K). These intercepts for the pure component in a specific crystal structure are called the lattice stability. In some cases they are real, in other cases they are inferred. One example is the bcc structure in the Al-Ni system above -- crystal bcc forms of pure aluminum or nickel do not exist.

The various lattice stabilities can be deduced in part from the characteristics of the phase diagram, measurements where the structure does exist (in this case an extensive solid solution) and trends in the periodic table. A great deal of work was originally conducted by Kaufman and co-workers and their lattice stabilities have formed the basis of phase diagram calculations to the present day.¹ In general, these lattice stabilities are relative to the liquid phase, are linear with temperature, and are of the form:

$$G = a + bT \quad (4)$$

where at the melting point, G is zero, a corresponds to the heat of fusion, and b the entropy of fusion. Hence there is no direct method of measuring lattice stabilities for pure elements in crystal forms that are not known to exist. Other terms for temperature can be added, but the linear treatment is usually sufficient over the temperature ranges under consideration.

The shape of the energy curve is also a function of the energy of mixing, and this accounts for the droop of the curve from a line connecting pure A to pure B for that particular phase. In general,

$$G^{mix} = \left(RT \sum x_i \ln(x_i) \right) + G^E \quad (5)$$

where the first term is the ideal energy of mixing assuming a perfectly random solution. The second term, G^E , is the excess energy of mixing which describes the extent of departure from the ideal situation. This term corresponds to the activity coefficient for a constituent in the solution and this quantity must be measured directly.

There are various ways to express the Gibbs excess energy as a function of composition. Although the form of these expressions may have a physical interpretation, the final form is always an analytical expression that gives the best fit for the data available.

Another constraint is that the expression must also obey the Gibbs-Duhem equation where:

$$\sum x_i d\bar{G}_i^E = 0 \quad (6)$$

This equation establishes a relationship between the partial molar excess Gibbs energies. The key point is to ensure that the partial and integral excess properties are expressed in equation forms where this relationship is obeyed. A commonly used formalism has been derived by Margules where the integral quantity, G^E , is expressed as:

$$G^E = x_A x_B (p_0 + p_1 x_B + p_2 x_B^2 + \dots + p_n x_B^n + \dots) \quad (7)$$

then the partial molar properties of components A and B are:

$$\bar{G}_A^E = x_B^2 \left((p_0 - p_1) + 2(p_1 - p_2)x_B + 3(p_2 - p_3)x_B^2 + \dots + ((n+1)(p_n - p_{n+1})x_B^n + \dots) \right) \quad (8)$$

$$\bar{G}_B^E = x_A^2 \left(p_0 + 2p_1 x_B + 3p_2 x_B^2 + \dots + (n+1)p_n x_B^n + \dots \right) \quad (9)$$

If p_0 is the only interaction parameter, the solution is said to be regular. If there are two parameters required, the solution is said to be sub-regular. The parameters, p_n , can vary with temperature in a manner similar to the lattice stabilities above. Here, a "cTlnT" term can be included to give a better fit over a wider range of temperatures. Historically, the temperature dependence has been expressed as a power series in T. Kaufman^{1,4} fit known data for several binary systems to an equation of the form:

$$G^{mix} = RT(x \ln(x) + (1-x) \ln(1-x)) + x(1-x)(g(T) + xh(T)) \quad (10)$$

where the first term is the ideal mixing energy and the $g(T)$ and $h(T)$ functions are in power series of temperature. Note that if $g(T)=h(T)$, the solution is regular. The FACT system, when calculating phase equilibria, does not allow the use of a power series as such equations usually do not extrapolate in a realistic manner. This can restrict the usefulness of these equations to temperature ranges where the excess properties are well known, and thus are of limited value.

Then for any binary solution phase of A and B, the Gibbs energy with respect to the standard state can be represented by the equation:

$$G = x_A(a + bT) + x_B(c + dT) + \left(RT \sum x_i \ln(x_i) \right) + x_A x_B (p_0 + p_1 x_B + p_2 x_B^2 + \dots + p_n x_B^n + \dots) \quad (11)$$

where the first two terms represent the lattice stabilities of component A and B respectively, and the corresponding partial molar properties are then represented by:

$$\overline{G}_A = (a + bT) + RT \ln(x_A) + x_B^2 \left[(p_0 - p_1) + 2(p_1 - p_2)x_B + 3(p_2 - p_3)x_B^2 + \dots + ((n+1)(p_n - p_{n+1})x_B^n) \right] \quad (12)$$

$$\overline{G}_B = (c + dT) + RT \ln(x_B) + x_A^2 \left[p_0 + 2p_1x_B + 3p_2x_B^2 + \dots + (n+1)p_nx_B^n \right] \quad (13)$$

The Phase Diagrams

Nickel - Chromium

The assessed Ni-Cr phase diagram² presented at Figure 3 shows four phases, three of which have been modelled in the literature. The fourth, unmodelled phase is a low temperature solution which first precipitates on cooling at 590°C as Ni₂Cr. An updated phase diagram assessment³ gives the parametric equations for a phase diagram consisting of three solution phases: liquid, Cr rich (bcc), and Ni rich (fcc). The assessor³ stated that he could not find, nor derive equations that result in a better representation of the diagram. The characteristic features of the diagram are preserved, although they may be out by as much as 50° as is the case for the eutectic temperature.

The first obstacle was that the list of parameters given in the original assessment was incomplete. Thus, the original treatment by Kaufman was obtained⁴ and it was further discovered that there was a typographical error in the coefficients as well. Moreover, the lattice stability parameters as given by Kaufman did not result in the observed melting points of the pure substances. This observation was also made in the updated assessment. For nickel, the heat of solidification was adjusted slightly to bring the melting point into agreement. However, for chromium, the melting point was out by over 35°. The FACT database also gave an erroneous melting point⁵. Three values for the heat of solidification were found in various references. They were 15313 J/mol (3660 cal/mol)⁶, 16900 J/mol⁷ and 21000 J/mol⁸. The median of 16900 J/mol was assumed and the resulting entropy of solidification was 7.912 J/molK. The lattice stability of fcc chromium with respect to the liquid phase was derived using the expression for the theoretical transformation of chromium from bcc to fcc as given by Kaufman⁹.

The excess energies were expressed in powers of temperature. These power series, as originally derived by Kaufman, were re-fit to the form of equation (4) above and included a "TlnT" term. These equations were then entered into the FACT module POTCOMP and the phase diagram was calculated. There is the ability within POTCOMP to enter the excess expressions in a power series and so a comparison of the resulting diagrams from the literature

and the equations developed under this project was made. The final parameters developed here are listed at Table 1 below. The diagram as calculated from the parameters given by Kaufman is attached at Figure 4 and the diagram from the current work is attached at Figure 5.

As mentioned above, the new lattice stabilities resulted in the correct melting points of the pure substances. Of interest is that in the extrapolation to lower temperatures, the new equations gave a more accurate representation of the solubility of chromium in nickel. The eutectic temperature increased slightly and the eutectic compositions moved closer to the experimentally observed values.

Nickel - Aluminum

The assessed phase diagram¹⁰ is attached as Figure 6. Several analytical treatments for this system exist and a very good representation has been made by Ansara et al¹¹ using a quasi-chemical model for the solid solution phases. This model can be used in the FACT system; however, when dealing with multi-component phase equilibria, each element requires two lattice stability parameters and then the associated interaction parameters. This greatly increases the number of parameters and each additional solute in the phase will result in an increasingly complex model. A simple solution model, although not perhaps as exact, can be used successfully to describe the thermodynamic properties of the system within experimental error. Thermodynamic data has been summarized by Desai¹² and was used in the development of the excess energy expressions for the liquid phase.

To facilitate the modelling of this diagram, the Al_3Ni phase was modelled as a stoichiometric compound with the Gibbs energy relative to the liquid phase. The extensive solid solution phase of NiAl was modelled first, following with the nickel rich side and finally the aluminum rich side.

The characteristic NiAl solid solution is believed to melt congruently at 50 at % at 1911K. Due to the asymmetry of the shape of the NiAl feature on the phase diagram, this treatment used a sub-regular solution model. It was found that by moving the congruent melting point to 54 at% nickel, the parameters in the sub-regular solution model became much more reasonable and realistic. This modelling procedure is described in greater detail at Annex A.

Once the NiAl phase was modelled, the fcc nickel solution was fit to a sub-regular solution model to give the eutectic feature at 1633 K. As a check, the fcc model was compared to the data given by Desai. As these reported values were consolidated from several other sources, Desai did note that other sources reported values that were less exothermic. The model derived in this work reproduced values that were consistently less exothermic, but well within the error limits, of those values given. It should be noted that the nickel and aluminum solid solutions both have the fcc structure. Hence, the related excess

energy equation is continuous as a function of composition and describes both the aluminum rich and nickel rich solid solutions.

The compounds were fit into the diagram in a manner similar to that for the solutions. On a composition versus energy graph, a stoichiometric compound is represented by a point and is treated in the same manner as a curve. If this compound is stable, then the point lies on a line that is tangent to an energy curve and this tangent represents the minimum Gibbs energy. If there are two stable compounds, as is found in this treatment of the nickel - aluminum phase diagram, then the line between the two points lies below all other energy curves. In Figure 7, the tangent A represents the phase diagram tie line between the liquid and the solid. Similarly, the tangent B represents a tie line between the Al_3Ni and Al_3Ni_2 compounds.

The last phase modelled was the fcc prime, AlNi_3 , phase. This was derived solely from the eutectic feature and the 1273K tie line between the fcc and fcc' phases. The energy of formation compared to literature values¹² are within 10%.

The parameters are listed at Table 2 below and the calculated phase diagram is attached at Figure 8.

Aluminum - Chromium

This phase diagram¹³ is attached at Figure 9 and is marked by an extensive solid solution on one side (chrome rich) and several intermetallic compounds on the other side (aluminum rich). The Ni-Al diagram is, by comparison, fairly symmetric. The aluminum-chrome system itself has been mentioned in the literature, commonly as the third side to a ternary phase diagram. Yet, no complete treatment could be found. Some parameters for the Cr rich side of the diagram were developed by Kaufman¹⁴ in the mid-1970's, but the treatment did not extend completely to the Al solid solution. Although a key part of the Ni-Al-Cr system, there is a surprising lack of assessments and good data in the literature. The Al-Cr binary diagram would prove to be the most challenging system to model of the three.

The only thermodynamic data for this system that could be found was compiled by Desai in Hultgren et al¹⁵. Similar to the start of the Ni-Al phase diagram, a regular solution expression for the Gibbs' excess energy of mixing for the Cr (bcc) solid solution was developed from this data. There are two basic approaches to modelling a phase diagram - start from one side, or start from a temperature and work up or down. The first attempt was to start at higher temperature and develop a liquid model that corresponds to the regular solution treatment for the bcc phase. Modelling the intermetallic phases as simple compounds, equations were derived to give the proper peritectic structure, starting from high temperature and working towards the aluminum region. Neither a simple regular nor sub-regular solution model for the liquid phase did not result in good agreement with the intermetallic compounds in the phase diagram. The deviation from observed features became unacceptable at the

aluminum side of the diagram. A similar approach was then attempted, but now modelling intermetallic compounds moving from the aluminum rich side into an area where the exact features of the phase diagram were not well known. This approach simply did not work. Besides a poor fit, the resulting intermetallic models indicated that an intermetallic compound would decompose into the two neighbouring intermetallic compounds at temperatures where this surely would have been observed by previous workers. These difficulties are further illustrated by an interim model at Annex B.

What turned out to be the successful approach was to derive a many-parameter model for the liquid phase based on the Gibbs energy of formation of the intermetallic phases compiled by Desai. However, data for the two intermetallic compounds, Al_7Cr and $\text{Al}_{11}\text{Cr}_2$, were not available. From the mathematical treatment above, the energies for the equilibrium phases must result in the lowest common tangent. Bounds were placed on the values for what the Gibbs energies could be by plotting the tabulated energies as a function of compositions and drawing the associated lowest common tangents. Assuming that the temperature dependence of the Gibbs energy for all of the intermetallic compounds are the same, probable Gibbs energies could be assigned. This behaviour of the intermetallic compounds with respect to temperature was examined and the entropy changes with respect to liquid were considered to be 0, 5, and 10 J/mole K.

From these intermetallic models, as many as nine equations for nine parameters were derived from features of the phase diagram to give a good indication of the shape of the energy of mixing as a function of both composition and temperature. Slight changes in the composition of some of the tie lines were investigated to smooth the curve. These final curves were then cast into a simpler expression for the liquid. The best fit occurred with the entropy change for all intermetallic compounds being 5 J/molK. The last step was to include the aluminum solution phase, necessitating small changes in the model treatment for the two aluminum rich intermetallic compounds. The last step was to adjust the models for the intermetallic compounds where their properties were known. Even with the adjustments, the models reproduce the known data within experimental error. The parameters for the Al-Cr system are given at Table 3 below and the calculated phase diagram is attached at Figure 10.

Applications

As mentioned at the introduction, this work establishes the foundation upon which more realistic thermodynamic calculations can be performed. Entering the excess energy and the compound parameters into the FACT database enables the ternary system to be approximated through the use of various mathematical models; the commonly employed models include the Toop, Kohler, and Muggianu⁵. But most importantly, multi-component multi-phase equilibria with the other compounds and solutions in the FACT database can be calculated. These calculations will then provide a direction to research, identifying areas and experiments where a few good data points would further extend the applicability and usefulness of these models. As such, the development of this model has just completed the

first step in an iterative process.

All modelling efforts start with simple and well defined situations. For example, surface oxide maps for a nickel rich alloy may be calculated; whether hot, dry, cold, wet, and in various chemical environments. The calculations for the surface oxide on a nickel 10at% Cr, 1at%Al alloy at 1200°C in air are given at Annex C. The resulting oxides can vary depending on how the calculations are performed and this gives a better understanding of what can impact the final equilibria and to what magnitude. The calculations are in moderate agreement with observations¹⁶ given that the excess energy for oxides is not available and kinetic factors, such as ternary diffusion phenomena, have not been considered.

Summary

The nickel-chromium, nickel-aluminum, and aluminum-chromium binary systems have been successfully modelled. The representative systems are in good agreement with the observed thermodynamic properties present in the literature.

Future work will add to these models. Calculations of the ternary phase diagram will be made using the various interpolation models. The results will then be compared to known properties and differences accounted for through the interpolation model, or the introduction of ternary interaction parameters. Longer term work will examine the influence of other transition elements and consider the inclusion of the ternary solution phases which are known to appear in many superalloy systems.

Acknowledgements

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Annexes

- Annex A: Interim Models in the Aluminum-Nickel System
- Annex B: Interim Models in the Aluminum-Chromium System
- Annex C: Calculation to Determine the Surface Oxide

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Table 1: Ni-Cr Parameters.

Reference phase: liquids of the pure components.

Units: Joules per mole atoms.

Phase Name	Parameter	a	b	c	x_{Ni}^i	x_{Cr}^j
Liquid	$G^0_{(Cr,L)}$	0	0	0	-	-
	$G^0_{(Ni,L)}$	0	0	0	-	-
	ΔG^E	-8368			1	2
		-8368			2	1
fcc (Ni)	$G^0_{(Cr,fcc)}$	-6439	8.542	0	-	-
	$G^0_{(Ni,fcc)}$	-17642.2	10.209	0	-	-
	ΔG^E	29078.8	-36.111	-0.004184	1	2
		-29204.3	9.6056	0.2013	2	1
bcc (Cr)	$G^0_{(Cr,bcc)}$	-16900	7.912		-	-
	$G^0_{(Ni,bcc)}$	-12049.9	9.163		-	-
	ΔG^E	53555	-27.196		1	2
		-13389	-2.092		2	1

Table 2: Al-Ni Parameters.

Reference phase: liquids of the pure components.

Units: Joules per mole atoms.

Phase Name	Parameter	a	b	x_{Al}^i	x_{Ni}^j
Liquid	$G^0_{(Al,L)}$	0	0	-	-
	$G^0_{(Ni,L)}$	0	0	-	-
	ΔG^E	-122109		1	1
fcc (Al) (Ni)	$G^0_{(Al,fcc)}$	-10711	11.475	-	-
	$G^0_{(Ni,fcc)}$	-17642.2	10.209	-	-
	ΔG^E	-131000		1	1
		70000		3	1
bcc (NiAl)	$G^0_{(Al,bcc)}$	59889.4	11.930	-	-
	$G^0_{(Ni,bcc)}$	-17600	11	-	-
	ΔG^E	-427038		1	1
		267371		2	1
Al_3Ni_2	$G^0(Al_{0.61}Ni_{0.39})$	-53090	10	-	-
Al_3Ni	$G^0(Al_{0.75}Ni_{0.25})$	-53079	21.45	-	-
(fcc') $AlNi_3$	$G^0(Al,fcc')$	95000	10	-	-
	$G^0(Ni,fcc')$	35000	0	-	-
	ΔG^E	-265693	-4.218	1	1
		-430066	112.817	1	3

Note: The NiAl phase, although listed as bcc, actually has a primitive cubic structure. Hence the lattice stability parameters are not identical to those used in the other phase diagrams.

Table 3: Al-Cr Parameters.

Reference phase: liquids of the pure components.

Units: Joules per mole atoms.

Phase Name	Parameter	a	b	x_{Al}^i	x_{Cr}^j
Liquid	$G^0_{(Al,L)}$	0	0	-	-
	$G^0_{(Cr,L)}$	0	0	-	-
	ΔG^E	107000	-10	1	1
		-17000		2	1
		-35000		7	1
		48000		1	3
fcc (Al)	$G^0_{(Al,fcc)}$	-10711	11.475	-	-
	$G^0_{(Cr,fcc)}$	-6439	8.542	-	-
	ΔG^E	-26400	-20	7	1
bcc (Cr)	$G^0_{(Al,bcc)}$	-627.6	6.6944	-	-
	$G^0_{(Cr,bcc)}$	-16900	7.912	-	-
	ΔG^E	-63000	-4.24	1	1
AlCr ₂	$G^0(Al_{0.333}Cr_{0.667})$	-35793	10	-	-
Al ₃ Cr ₂	$G^0(Al_{0.6}Cr_{0.4})$	-31000	5	-	-
Al ₂ Cr	$G^0(Al_{0.667}Cr_{0.333})$	-28200	5	-	-
Al ₄ Cr	$G^0(Al_{0.8}Cr_{0.2})$	-20760	5	-	-
Al ₁₁ Cr ₂	$G^0(Al_{0.846}Cr_{0.154})$	-18307	5.5	-	-
Al ₇ Cr	$G^0(Al_{0.875}Cr_{0.125})$	-16850	6.3	-	-

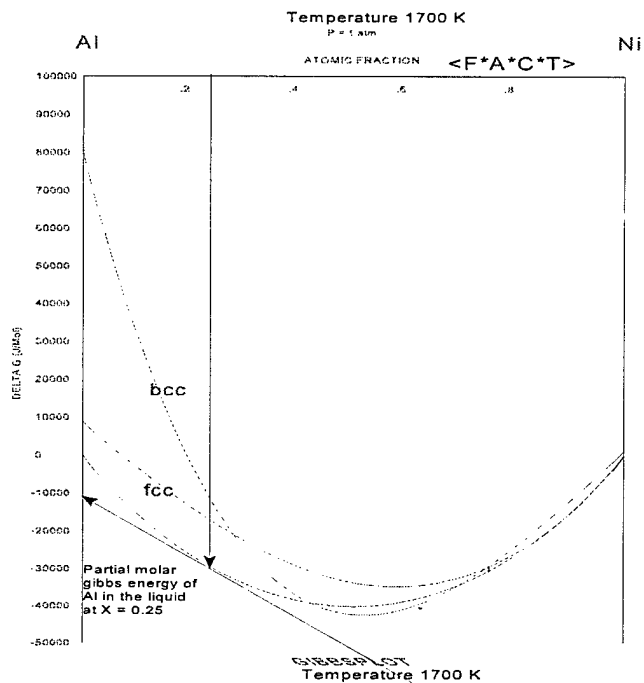


Figure 1: Energy vs composition for Al-Ni solution phases; bcc, fcc, and liquid at 1700 K.

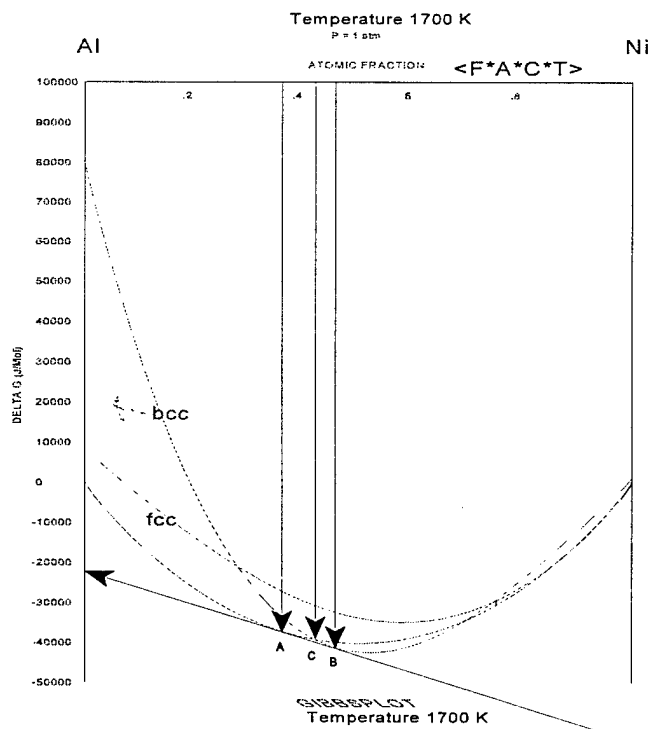


Figure 2: As in Figure 1, showing the lowest common tangent at system composition C.

Assessed Ni-Cr Phase Diagram

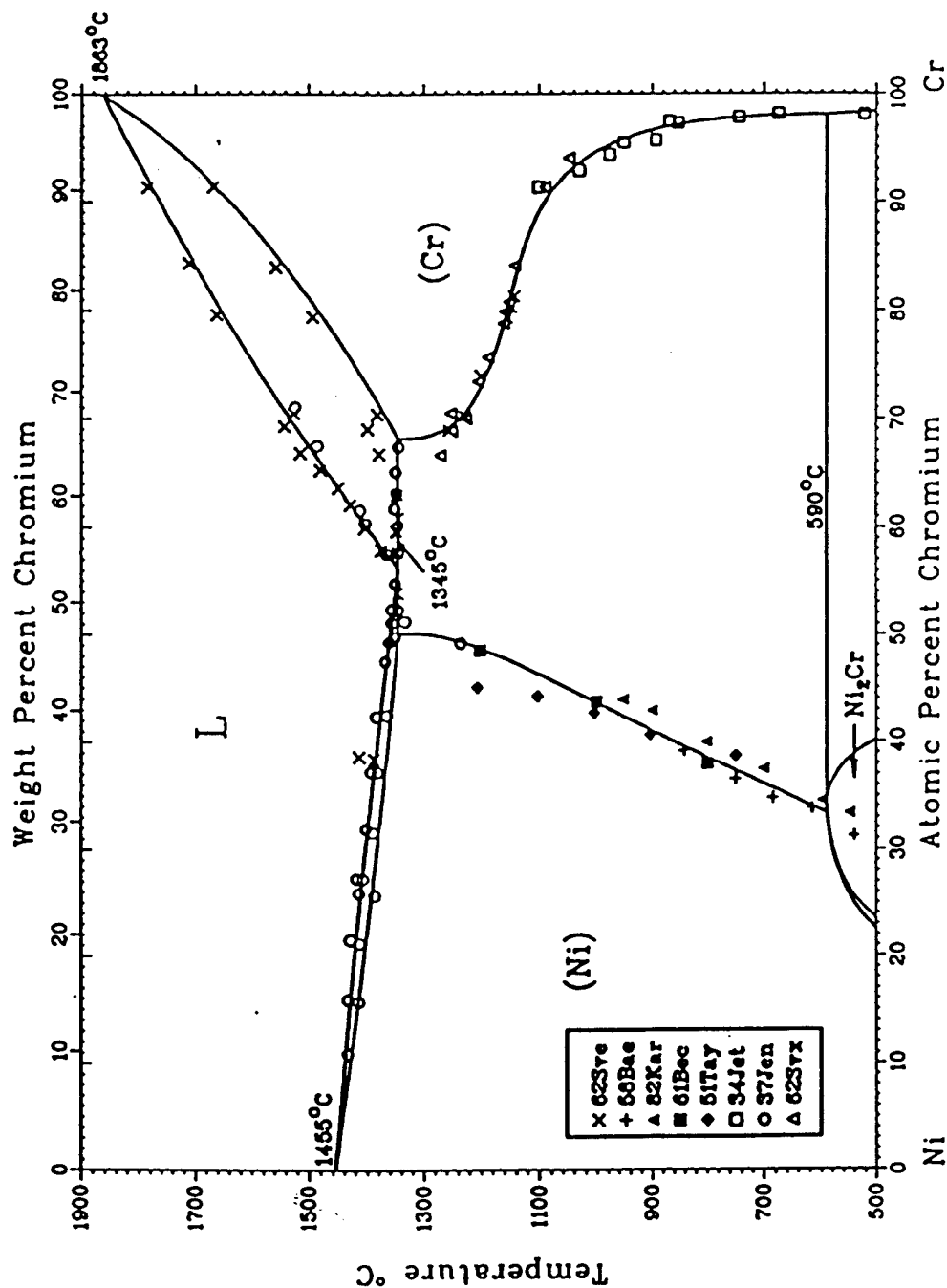


Figure 3: from reference 1.

Figure 4: Cr-Ni Phase Diagram calculated from reference 3.

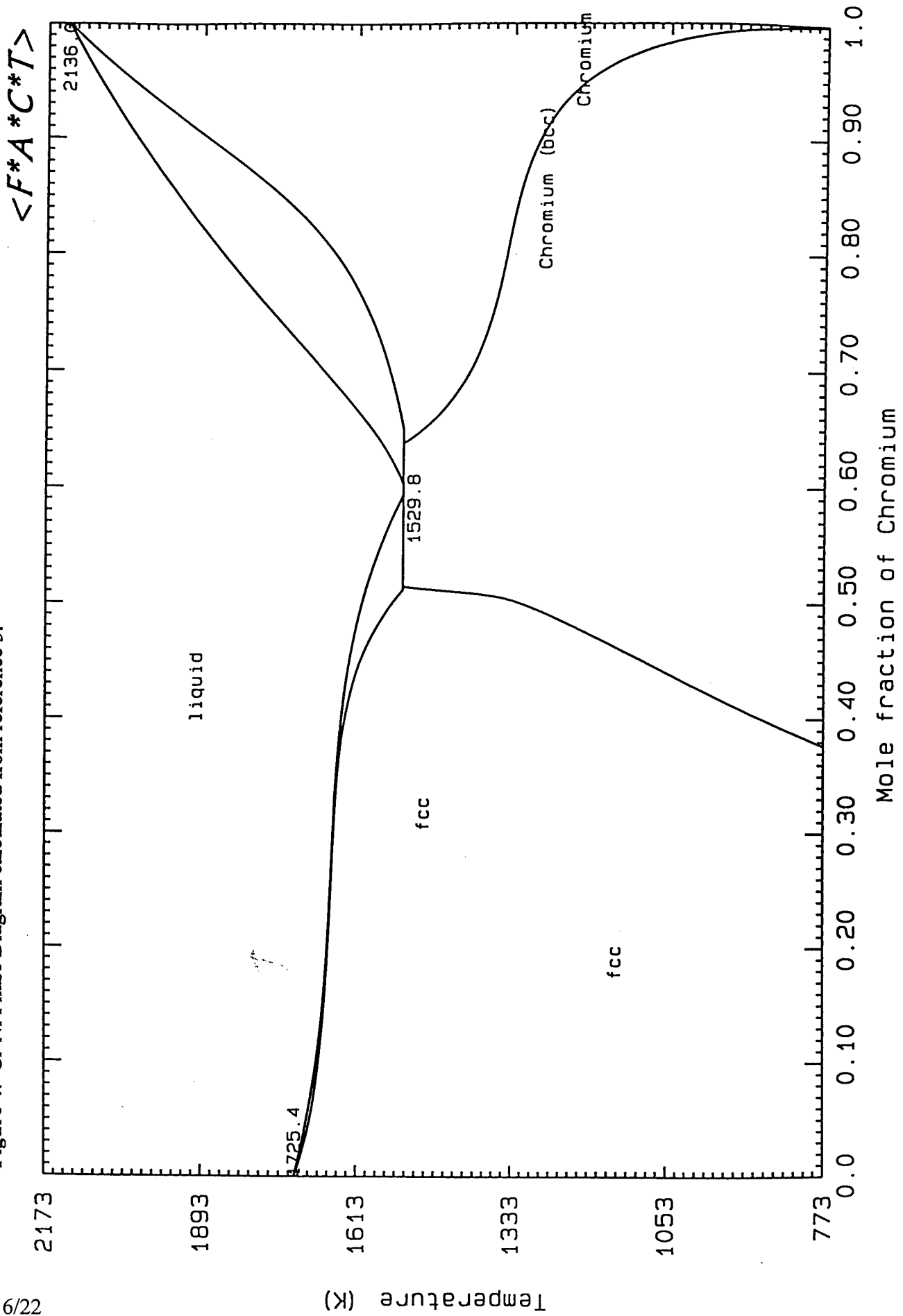
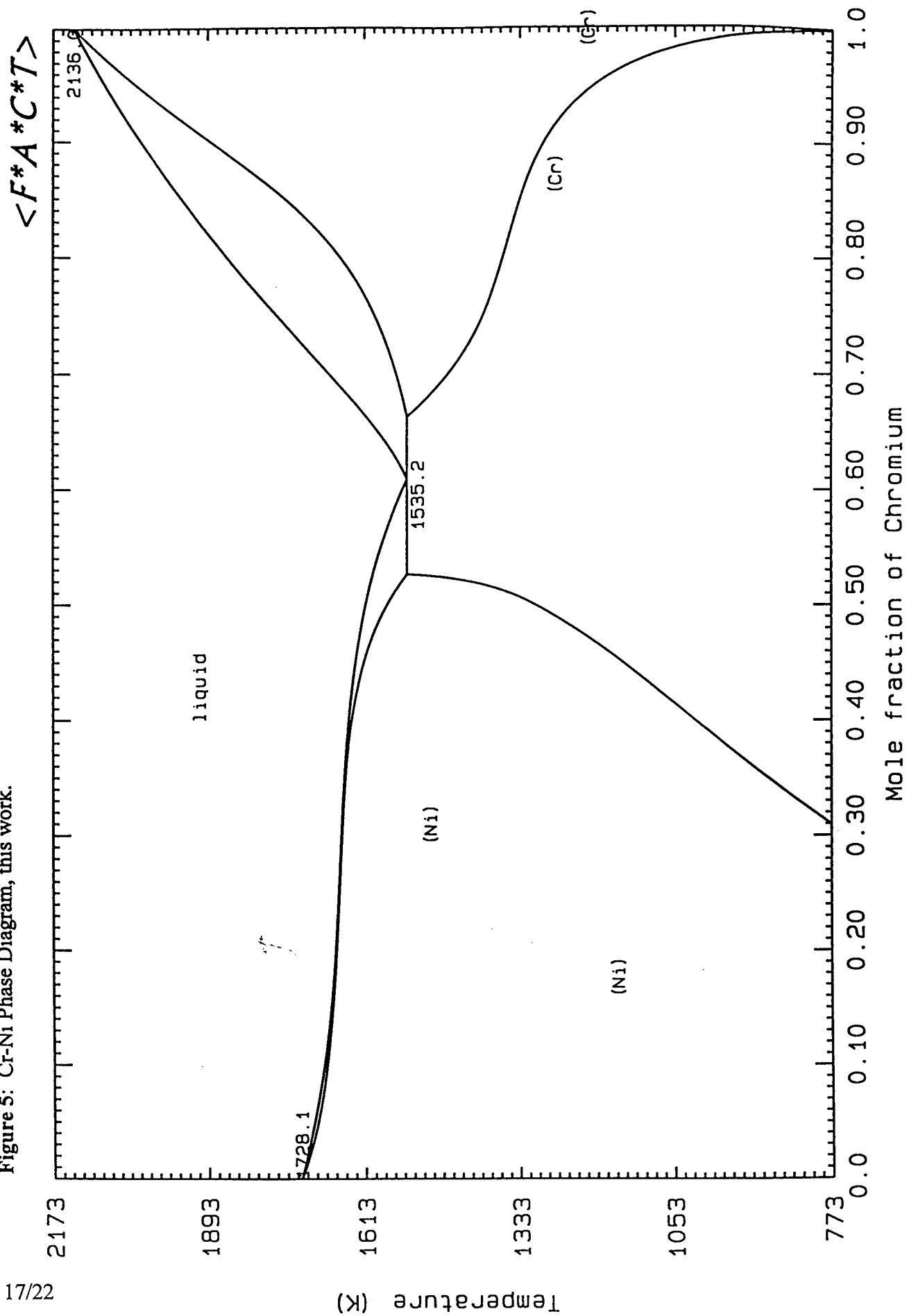


Figure 5: Cr-Ni Phase Diagram, this work.



Assessed Al-Ni Phase Diagram

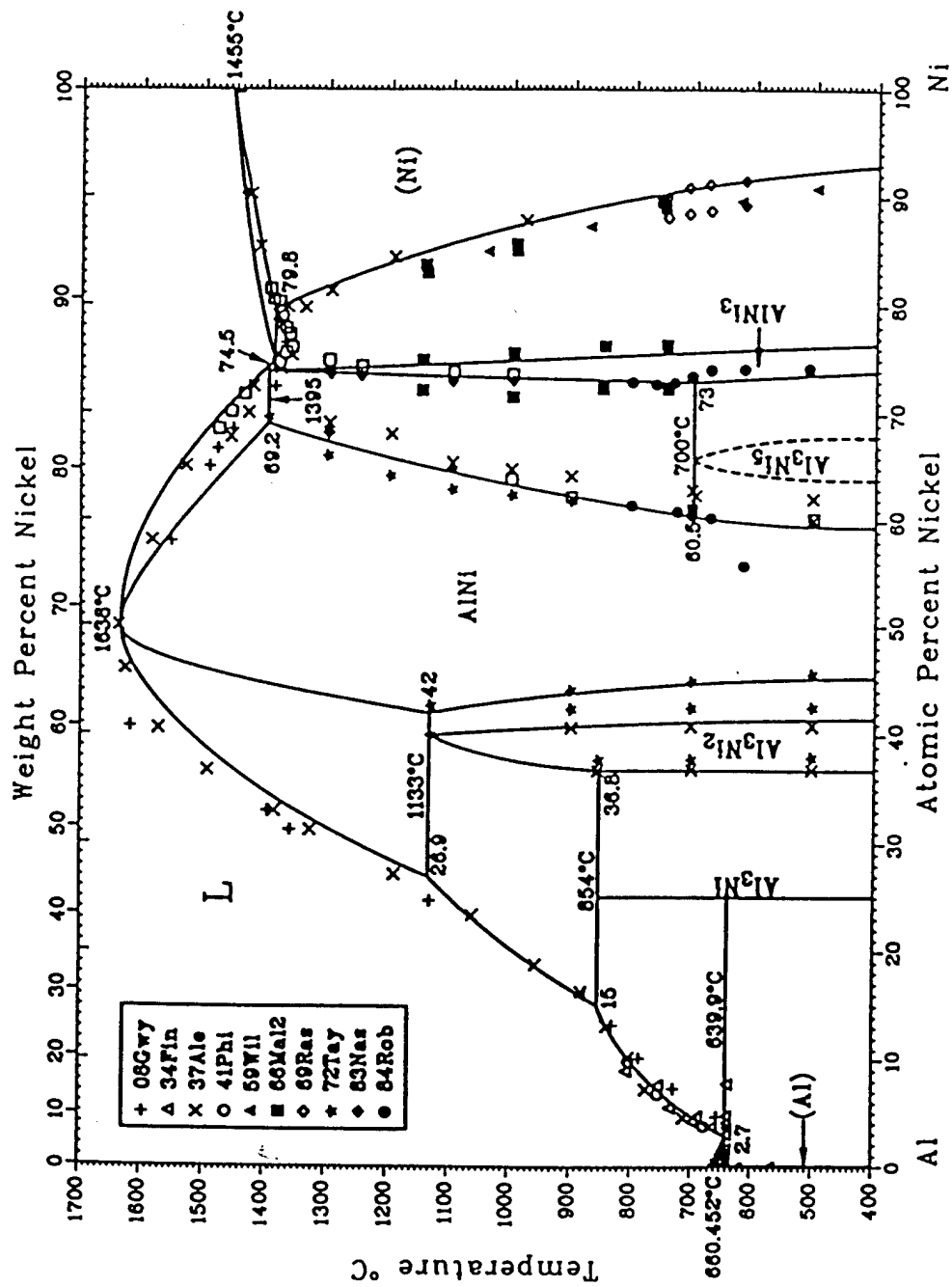


Figure 6: from reference 9.

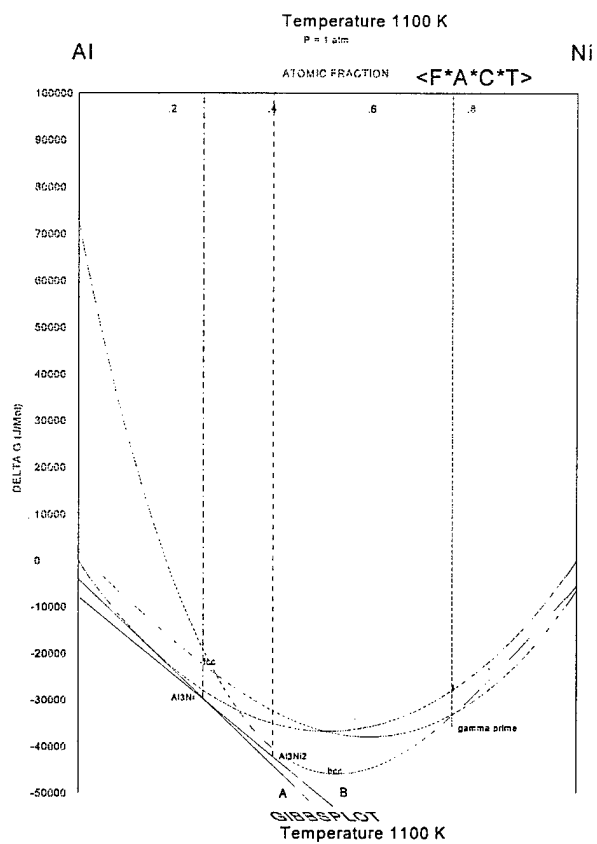
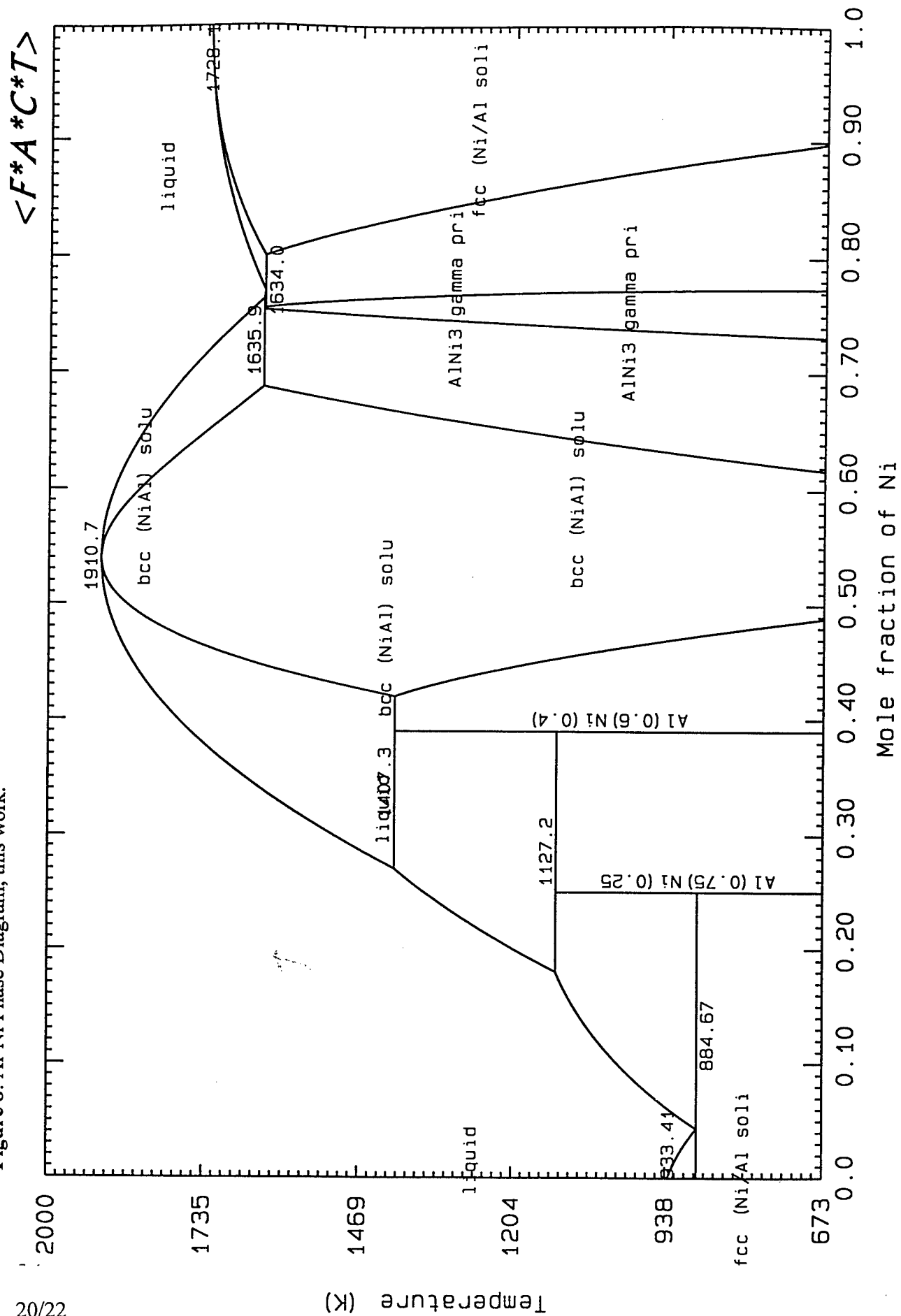


Figure 7: Energy vs Composition for the Ni-Al system at 1100 K.

Figure 8: Al-Ni Phase Diagram, this work.



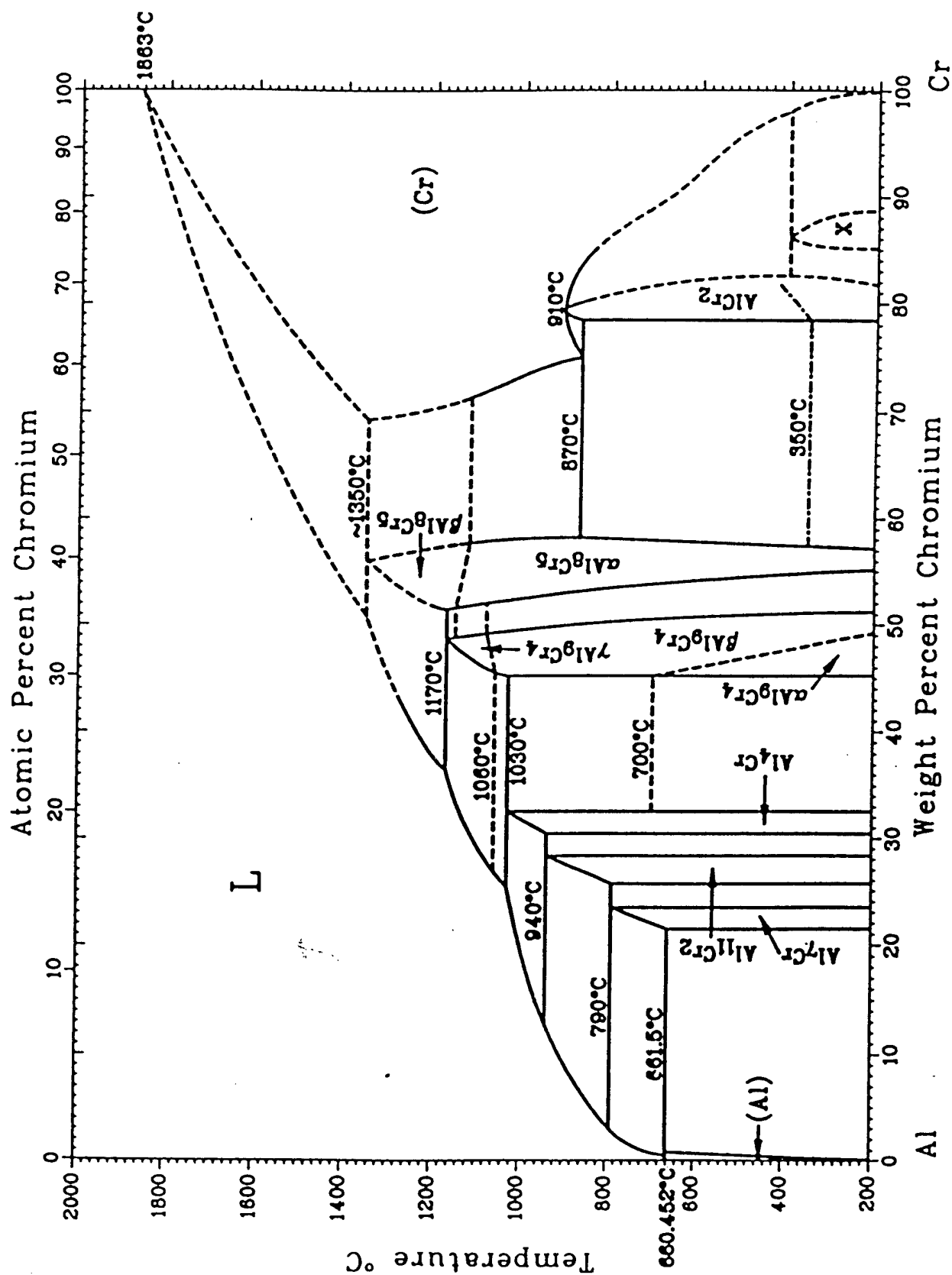
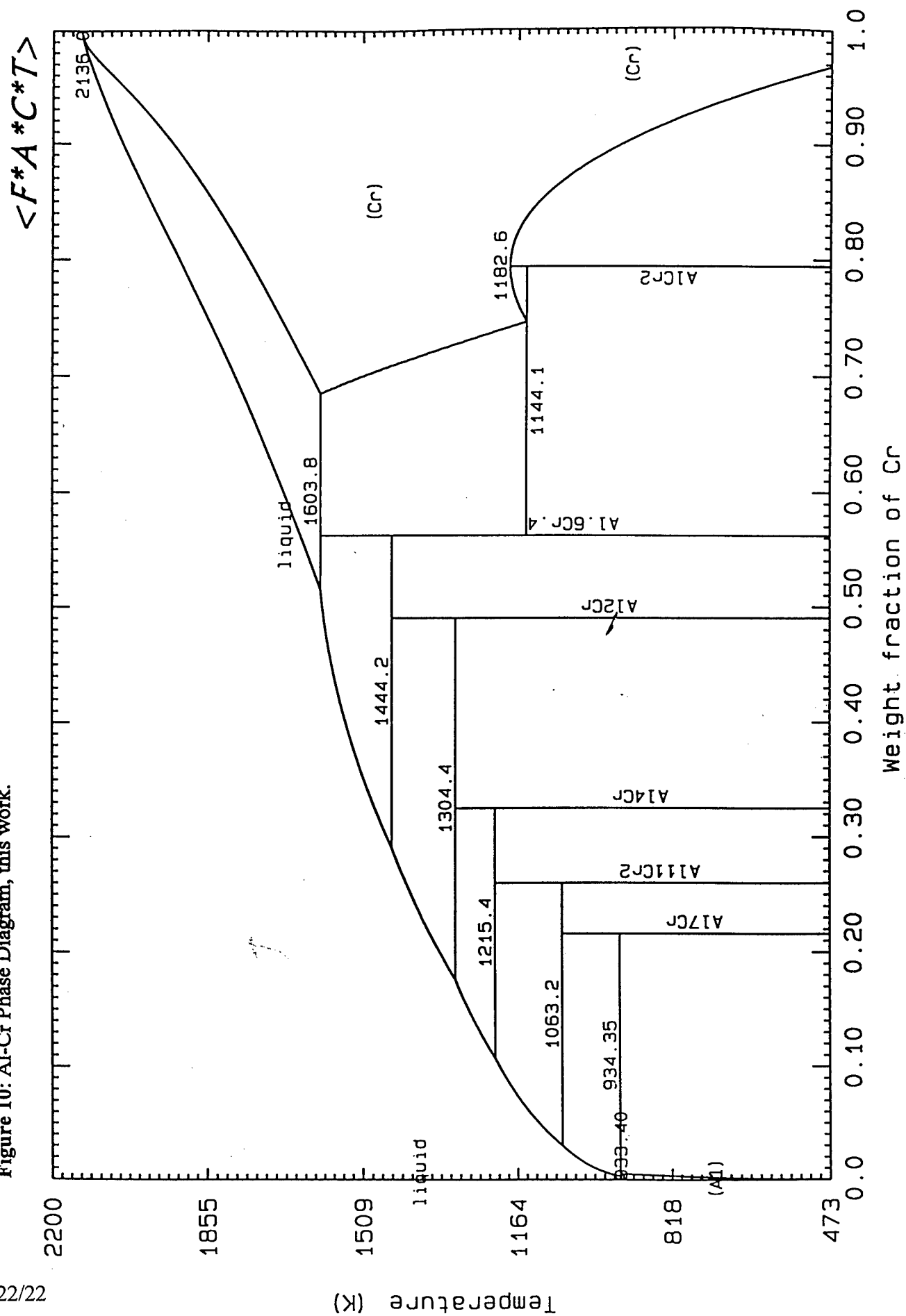


Figure 9: from reference 12

Figure 10: Al-Cr Phase Diagram, this work.



ANNEX A

Interim Models in the Aluminum-Nickel System

The development of the sub-regular solution model for the NiAl phase is a typical example of how parameters for various models can be fit to features of a phase diagram. As a tie line on the phase diagram represents the lowest common tangent on an energy versus composition plot, then one tie line can be used to derive two expressions equating the partial molar energies of each component in the different phases. From this, any even number of parameters can be solved uniquely.

First, the expression for the Gibbs excess energy for the liquid phase was derived from the data compiled by Desai¹. The liquid was assumed to be a regular solution and the parameter p_0 was fit to the data within experimental error. The temperature dependence of this parameter was assumed to be zero. With this expression, the partial molar Gibbs energy of both elements in the liquid phase could then be calculated. At equilibrium, as the partial molar energy for any component is the same all phases, tie lines on the phase diagram can be identified and used to solve for the selected parameters, as represented by equations 12 and 13, in the other phase.

For the NiAl solution phase, the lattice stability for primitive cubic nickel was first assumed to be that for bcc nickel as derived by Kaufman². The unknowns were taken to be the lattice stability parameters for aluminum in the primitive cubic structure and a sub-regular solution model for the NiAl phase. The NiAl solution phase itself was modelled as a sub-regular solution expanded in mole fraction of nickel. A short Excel spreadsheet was created that would solve the four equations with four unknowns and different forms of the sub-regular solution model could be easily accommodated. This also enabled a systematic examination of the effects on the magnitude of the parameters when the constraints were changed.

The partial molar equations were solved using the constraints of the tie line at 1406 K where $X_{\text{Ni}}^{\text{L}}=0.27$ and $X_{\text{Ni}}^{\text{bcc}}=0.48$ and the maximum melting point of 1911 K where $X_{\text{Ni}}^{\text{L}}=X_{\text{Ni}}^{\text{bcc}}=0.50$. The difficulty was that this feature is asymmetric with temperature - on the phase diagram, the aluminum side drops faster than the nickel side. This would indicate that on an energy versus composition diagram, the lattice stability for aluminum would be very positive. However in modelling this feature, the resulting parameters were not in keeping with what could normally be expected and that the liquidus and solidus on the nickel side were still falling off too steeply. As the maximum in the melting point moves from 0.50 to 0.54 mole fraction of nickel, the parameters change by a great deal and they gave the general shape of the liquid-NiAl feature. To improve the accuracy of the eutectic feature at 1633 K, the lattice stability of nickel was adjusted and the parameters re-calculated to those in the last row in Table A-1.

ANNEX A

Table A-1: Parameters as a Function of Composition.

Maximum	a	b	p0	p1
0.50	90315.2	10.64	-564669	420718
0.52	71751.3	12.12	-486185	327284
0.54	58464.6	13.62	-432995	263963
0.54	59889.4	11.93	-427038	267371

From the above table, a relatively small change in composition can have a significant effect on the magnitude of the parameters. Also, assuming a different expression for the solution phase would have generated different parameters with different sensitivity to changes in composition or temperature. It is then important to consider the form of the excess energy expression as well as examine the impact of a slight change in composition.

References

1. P.D. Desai, *J Phys Chem Ref Data*, 16 (1987) pp. 109-124.
- 2.L. Kaufman and H. Nesor, *Z Metall*, 64 (1973) pp 249-257.

ANNEX B

Interim Models in the Aluminum-Chromium System

This phase diagram posed great difficulty in deriving expressions that gave a suitable representation of the intermetallic compounds. When one expression resulted in the liquidus being in the correct position, the resulting temperature dependence in another expression resulted in drastically different behaviour in another region of the diagram at temperatures where this behaviour would have surely been observed and reported.

In general, the Gibbs energies for the compounds can be calculated exactly, relative to the liquid phase, in a manner similar to that for two solutions in equilibrium. At the liquidus composition, the tangent to the energy curve must pass through the point which represents the Gibbs energy for the compound. The energy for the compound is then:

$$G_{A,B(1-x)}^{solid} = x \overline{G}_A^{liq} + (1-x) \overline{G}_B^{liq}$$

Note that the \overline{G}^{liq} terms above are calculated at the liquidus composition. The temperature dependence can be derived by calculating the energy at a different temperature and liquidus composition.

The chromium solid solution and the $AlCr_2$ intermetallic were modelled on the information compiled by Desai¹ and these parameters did not change significantly throughout this development. The liquid model was then derived from the tie line at 1625 K and that there was a smooth and gradual separation of the liquidus and solidus to this line. The remaining intermetallic compounds were modelled moving from the peritectic at 1625 K towards the aluminum side of the diagram. The compound parameters below in Table B-1 were solved exactly from the method given above.

The phase diagram which is derived from this model, less the compound $Al_{11}Cr_2$, is attached at Figure B-1. The liquidus points are preserved, but the model fails at lower temperatures. Including the expression for $Al_{11}Cr_2$ results in the diagram at Figure B-2 where two intermetallic compounds decompose. Several different models for the liquid phase were assumed, but all resulted in either the liquidus not being far enough to the left or eutectic decomposition at high temperatures.

The liquid phase could not be treated with an assumed, simple two or three parameter model over the entire range of composition. An alternative approach used was to derive expressions for the intermetallic compounds from the literature and then fit a curve through selected peritectic features. Note that each peritectic is described by four equations, not just

ANNEX B

two. The resulting complex liquid model was then simplified as the behaviour of the liquid phase was now apparent.

Table B-1: Al-Cr Parameters - Interim Model.

Reference phase: liquids of the pure components.

Units: Joules per mole atoms.

Phase Name	Parameter	a	b	x_{Al}^i	x_{Cr}^j
bcc (Cr)	$G^0_{(Al,bcc)}$	-627.6	6.6944	-	-
	$G^0_{(Cr,bcc)}$	-16900	7.912	-	-
	G^E	-63000	-4.24	1	1
$AlCr_2$	$G^0(Al_{0.333}Cr_{0.667})$	-35793	10	-	-
Liquid	$G^0_{(Al,L)}$	0	0	-	-
	$G^0_{(Cr,L)}$	0	0	-	-
	G^E	45000	-50	1	1
		-85000		3	1
		60000		4	1
Al_3Cr_2	$G^0(Al_{0.6}Cr_{0.4})$	-24826	1.633	-	-
Al_2Cr	$G^0(Al_{0.667}Cr_{0.333})$	-19681	0	-	-
Al_4Cr	$G^0(Al_{0.8}Cr_{0.2})$	-16281	2.622	-	-
$Al_{11}Cr_2$	$G^0(Al_{0.846}Cr_{0.154})$	-14911	3.913	-	-

Reference

1. R. Hultgren, P.D. Desai, D.T.Hawkins, M. Gleiser, K.K. Kelley, Selected Values of the Thermodynamic Properties of Binary Alloys, ASM International (Metals Park, Ohio) 1973, pp.147-150.

ANNEX B

Figure B-1: Al-Cr interrim phase diagram showing decomposition of Al_2Cr .

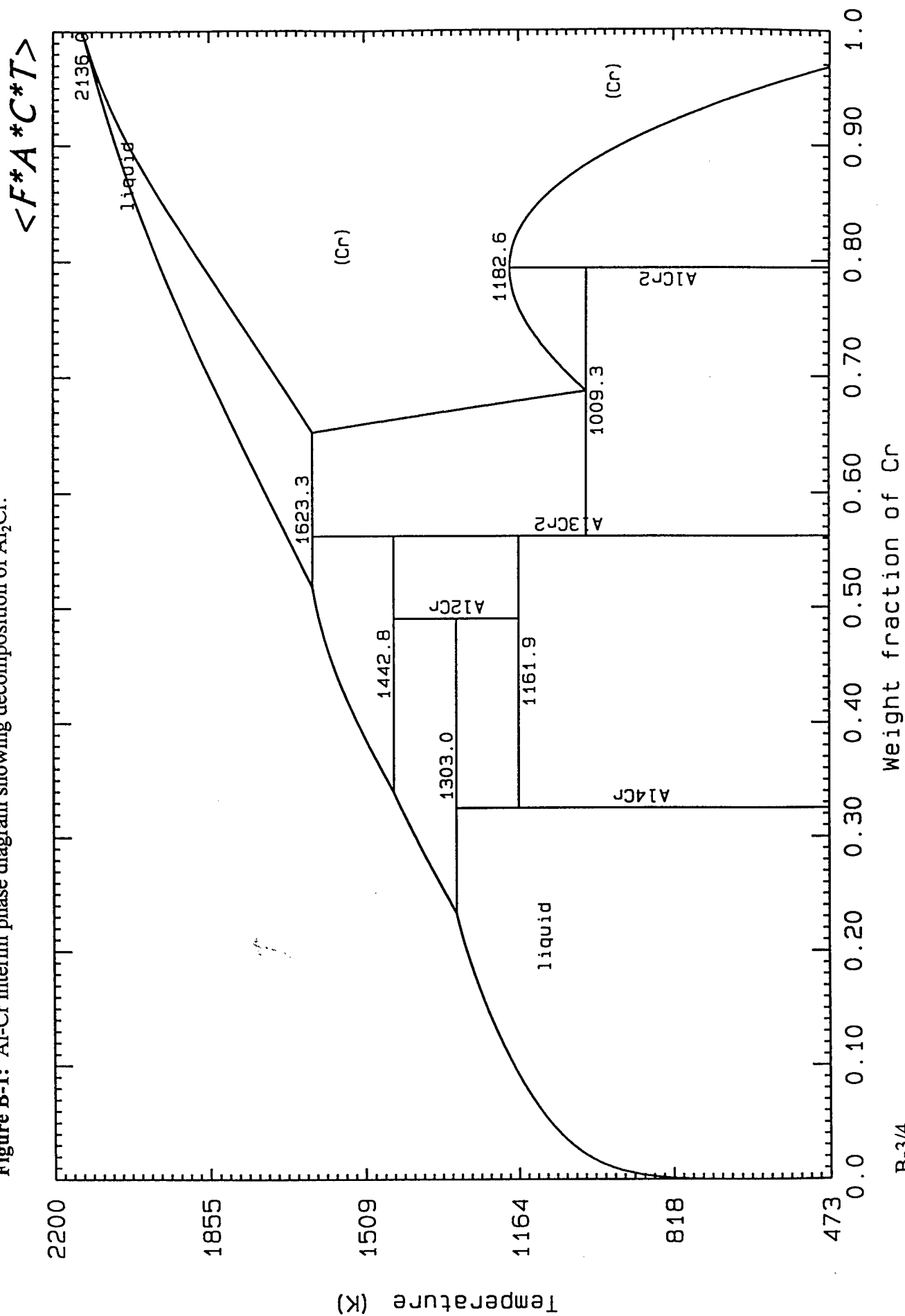
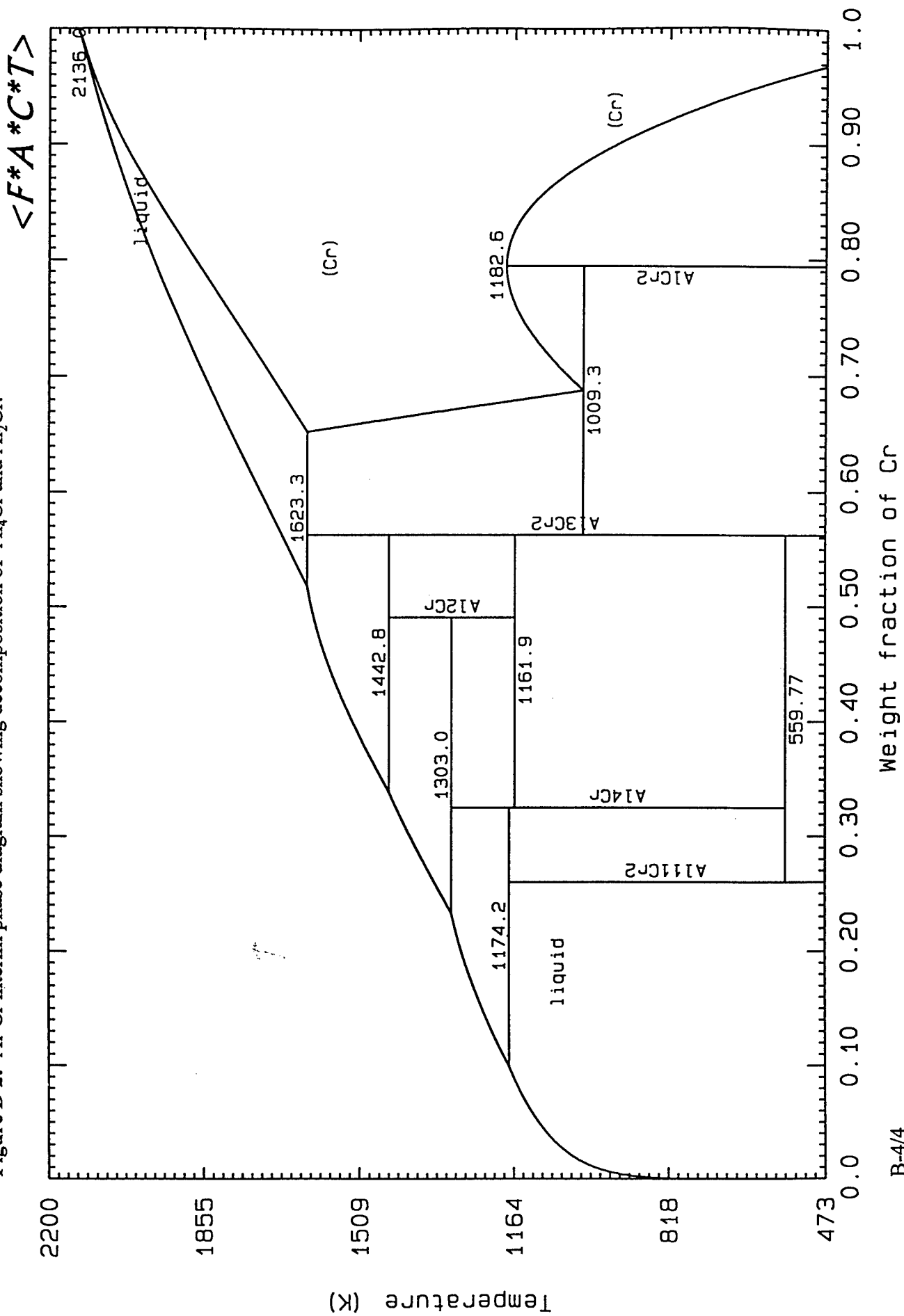


Figure B-2: Al-Cr interim phase diagram showing decomposition of Al_4Cr and Al_2Cr .

Annex C

Calculation to Determine the Surface Oxide

The following calculations are an example of how the composition of the oxide scale on a nickel chrome aluminum alloy may be determined from thermodynamic equations. The FACT module EQUILIB determines the equilibrium phase composition and mass balance of the final products as selected by the user. As the Gibbs energy is an extensive property, the calculations are done in a closed system. To input a system representing the oxide scale, consider one mole of a nickel 10at%Cr, 1at%Al alloy with 0.01 moles of air at 1200°C. Note that the equilibrium compositions are independent of the initial states of the reactants. Each calculation below considers a different selection of final phases. In each selection, however, the product gas is treated as an ideal solution.

This first calculation considers the solid products contained in the FACT database. This includes slag and corundum solutions, but no alloys. The solids are considered as a mechanical mixture of compounds and only those are listed where the activity is greater than $10e^{-30}$. As seen in the output below, the air would completely react with the alloy and the products would be corundum (Al_2O_3/Cr_2O_3 solution) Ni, Cr, Cr_2N , and AlN . These results are not realistic as the binary phase diagram Ni-Cr shows that the stable phase at 1200°C is a solid solution. From the Ni-Al phase diagram, aluminum is also soluble in nickel. Also, metal nitrides are generally not formed this easily. Of note is that the corundum solution is slightly favoured over the pure Al_2O_3 . This is consistent with the result that the mole fraction of Al_2O_3 in corundum is very low.

Output 1

DND/AIR VEHICLE RESEARCH SECTOR

0.89 Ni + 0.1 Cr + 0.01 Al +

.0079N2 + 0.0021 O2

=

0.00000	mol	(0.30116E-01	N2
		+	0.21767E-06	Cr
		+	0.28040E-07	Ni
		+	0.13784E-09	Al
		+	0.22605E-11	Al2O
		+	0.65974E-12	CrO
		+	0.61267E-13	CrN
		+	0.54872E-14	AlO
		+	0.52033E-14	N
		+	0.43538E-14	NO
		+	0.24436E-16	O
		+	0.21846E-16	NiO
		+	0.25650E-17	(AlO)2
		+	0.20455E-17	CrO2
		+	0.24157E-18	Al2
		+	0.66532E-19	AlN
		+	0.46427E-19	N2O
		+	0.97585E-20	N3
		+	0.77288E-22	O2
		+	0.57475E-23	AlO2
		+	0.38983E-26	CrO3

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```

+ 0.46600E-27      NO2)
  ( 1200.00 C, 1.0000      atm, gas_ideal, a=0.30116E-01)

+ 0.00000      mol  ( 0.18873      Al2O3      :Slag solution from FACT database,
+ 0.16353E-03      CrO      Activity = 0.1889 wrt
+ 0.81240E-05      Cr2O3)      phases present
  ( 1200.00 C, 1.0000      atm, Slag-liq, a=0.18890      )

+ 0.14000E-02 mol  ( 0.99991      Al2O3      :Corundum sol'n from FACT database
+ 0.85706E-04      Cr2O3)      atm, Corundum)
  ( 1200.00 C, 1.0000

+ 0.89000      mol Ni
  ( 1200.00 C, 1.0000      atm, S1, a= 1.0000      )

+ 0.82800E-01 mol Cr
  ( 1200.00 C, 1.0000      atm, S1, a= 1.0000      )

+ 0.85998E-02 mol Cr2N
  ( 1200.00 C, 1.0000      atm, S1, a= 1.0000      )

+ 0.72002E-02 mol AlN
  ( 1200.00 C, 1.0000      atm, S1, a= 1.0000      )

+ 0.00000      mol Al2O3
  ( 1200.00 C, 1.0000      atm, S4, a=0.99983      )

+ 0.00000      mol Ni
  ( 1200.00 C, 1.0000      atm, L1, a=0.81424      )

+ 0.00000      mol Al2O3
  ( 1200.00 C, 1.0000      atm, S2, a=0.62605      )

+ 0.00000      mol Al2O3
  ( 1200.00 C, 1.0000      atm, S3, a=0.58248      )

+ 0.00000      mol Ni3Al
  ( 1200.00 C, 1.0000      atm, S1, a=0.57773      )

+ 0.00000      mol Cr
  ( 1200.00 C, 1.0000      atm, L1, a=0.53979      )

+ 0.00000      mol Al2O3
  ( 1200.00 C, 1.0000      atm, S1, a=0.41508      )

+ 0.00000      mol CrN
  ( 1200.00 C, 1.0000      atm, S1, a=0.29593      )

+ 0.00000      mol NiAl
  ( 1200.00 C, 1.0000      atm, S1, a=0.44865E-01)

+ 0.00000      mol Al2O3
  ( 1200.00 C, 1.0000      atm, L1, a=0.31924E-01)

+ 0.00000      mol NiAl
  ( 1200.00 C, 1.0000      atm, L1, a=0.14153E-01)

+ 0.00000      mol CrO
  ( 1200.00 C, 1.0000      atm, L1, a=0.96233E-03)

+ 0.00000      mol Al

```


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```

( 1200.00 C, 1.0000      atm, L1, a=0.16334E-04)
+ 0.00000      mol Al      T
  ( 1200.00 C, 1.0000      atm, S1, a=0.10170E-04)
+ 0.00000      mol Ni2Al3   T
  ( 1200.00 C, 1.0000      atm, S1, a=0.71541E-06)
+ 0.00000      mol (NiO) (Al2O3)
  ( 1200.00 C, 1.0000      atm, S1, a=0.33485E-06)
+ 0.00000      mol Cr2O3
  ( 1200.00 C, 1.0000      atm, S1, a=0.26516E-06)
+ 0.00000      mol NiO
  ( 1200.00 C, 1.0000      atm, S3, a=0.68552E-07)
+ 0.00000      mol NiO
  ( 1200.00 C, 1.0000      atm, L1, a=0.13715E-07)
+ 0.00000      mol NiO      T
  ( 1200.00 C, 1.0000      atm, S2, a=0.73841E-08)
+ 0.00000      mol NiO      T
  ( 1200.00 C, 1.0000      atm, S1, a=0.53472E-08)
+ 0.00000      mol Cr2O3
  ( 1200.00 C, 1.0000      atm, L1, a=0.37994E-08)
+ 0.00000      mol CrO2      T
  ( 1200.00 C, 1.0000      atm, S1, a=0.12128E-08)
+ 0.00000      mol Cr3O4
  ( 1200.00 C, 1.0000      atm, S1, a=0.39714E-09)
+ 0.00000      mol NiAl3     T
  ( 1200.00 C, 1.0000      atm, S1, a=0.56688E-10)
+ 0.00000      mol (NiO) (Cr2O3)
  ( 1200.00 C, 1.0000      atm, S1, a=0.49316E-13)
+ 0.00000      mol CrO3      T
  ( 1200.00 C, 1.0000      atm, L1, a=0.14310E-23)
+ 0.00000      mol CrO3      T
  ( 1200.00 C, 1.0000      atm, S1, a=0.12531E-25)

```

The cutoff concentration has been specified to 1.000E-30
 Data on 8 product species identified with "T" have been extrapolated

The second calculation considers the final solid product assembly to possibly consist of all the solution phases in the FACT database plus the Ni fcc solution, the Cr bcc solution, the liquid alloy, and a mechanical mixture of the solid phases. For brevity, the product list has been cut off at an activity of $10e^{-6}$.

The resulting products consist of the gas phase, the corundum solution rich in Al_2O_3 , an alloy that is reduced in Al content, and AlN. The partial pressure of oxygen decreases as it

Annex C

is consumed in the formation of the oxides, and some nitrogen has reacted to form AlN to the extent where the activity of aluminum in the alloy is in equilibrium with the AlN. This is a result of the calculations based on the closed system. In all, this is much more reasonable result, confirming that the alloy is stable over the pure solids.

Output 2

DND/AIR VEHICLE RESEARCH SECTOR

0.89 Ni + 0.1 Cr + 0.01 Al +

.0079N2 + 0.0021 O2

=

```

0.43694E-02 mol ( 1.0000      N2
                  + 0.25127E-07 Ni
                  + 0.20493E-07 Cr
                  + 0.23921E-10 Al
                  + 0.21881E-12 Al2O
                  + 0.19965E-12 CrO
                  + 0.80640E-13 NO
                  + 0.33238E-13 CrN
                  + 0.29984E-13 N
                  + 0.30607E-14 AlO
                  + 0.78542E-16 O
                  + 0.62924E-16 NiO
                  + 0.49552E-17 N2O
                  + 0.19897E-17 CrO2
                  + 0.18672E-17 N3
                  + 0.79808E-18 (AlO)2
                  + 0.66532E-19 AlN
                  + 0.72750E-20 Al2
                  + 0.79850E-21 O2
                  + 0.10305E-22 AlO2
                  + 0.27743E-25 NO2
                  + 0.12188E-25 CrO3)
                  ( 1200.00 C, 1.0000 atm, gas_ideal)

+ 0.00000 mol ( 0.18879      Al2O3
                  + 0.49280E-04 CrO
                  + 0.44068E-05 Cr2O3)
                  ( 1200.00 C, 1.0000 atm, Slag-liq, a=0.18885 )

+ 0.14000E-02 mol ( 0.99995      Al2O3
                  + 0.46491E-04 Cr2O3)
                  ( 1200.00 C, 1.0000 atm, Corundum)

+ 0.99014 mol ( 0.89886      Ni
                  + 0.10100      Cr
                  + 0.14022E-03 Al
                  ( 1200.00 C, 1.0000 atm, fcc)
                  <--s :Solution
                  <--s model for
                  <--s) fcc nickel

+ 0.00000 mol ( 0.74827      Ni
                  + 0.73305E-01 Cr
                  + 0.83609E-02 Al
                  ( 1200.00 C, 1.0000 atm, L-NiCrAl, a=0.82994 )
                  <--s :Molten alloy
                  <--s
                  <--s)

+ 0.00000 mol ( 0.69915      Ni
                  + 0.13740      Cr
                  + 0.30652E-05 Al
                  ( 1200.00 C, 1.0000 atm, bcc, a=0.83656 )
                  <--s :chrome rich
                  <--s phase (bcc)
                  <--s)

```

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```

+ 0.70613E-02 mol AlN
( 1200.00 C, 1.0000 atm, S1, a= 1.0000 )

+ 0.00000 mol Al2O3
( 1200.00 C, 1.0000 atm, S4, a=0.99991 )

+ 0.00000 mol Ni
( 1200.00 C, 1.0000 atm, S1, a=0.89611 )

+ 0.00000 mol Ni
( 1200.00 C, 1.0000 atm, L1, a=0.72965 )

+ 0.00000 mol Al2O3
( 1200.00 C, 1.0000 atm, S2, a=0.62609 )

+ 0.00000 mol Al2O3
( 1200.00 C, 1.0000 atm, S3, a=0.58252 )

+ 0.00000 mol Al2O3
( 1200.00 C, 1.0000 atm, S1, a=0.41511 )

+ 0.00000 mol Ni3Al
( 1200.00 C, 1.0000 atm, S1, a=0.21022 ) <---

+ 0.00000 mol CrN
( 1200.00 C, 1.0000 atm, S1, a=0.16055 )

+ 0.00000 mol Cr
( 1200.00 C, 1.0000 atm, S1, a=0.94148E-01)

+ 0.00000 mol Ni3Al
( 1200.00 C, 1.0000 atm, S1, a=0.72144E-01)

+ 0.00000 mol Cr2N
( 1200.00 C, 1.0000 atm, S1, a=0.51077E-01)

+ 0.00000 mol Cr
( 1200.00 C, 1.0000 atm, L1, a=0.50820E-01)

+ 0.00000 mol Al2O3
( 1200.00 C, 1.0000 atm, L1, a=0.31927E-01)

+ 0.00000 mol NiAl
( 1200.00 C, 1.0000 atm, S1, a=0.69770E-02)

+ 0.00000 mol NiAl
( 1200.00 C, 1.0000 atm, L1, a=0.22009E-02)

+ 0.00000 mol CrO
( 1200.00 C, 1.0000 atm, L1, a=0.29121E-03)

+ 0.00000 mol Al
( 1200.00 C, 1.0000 atm, L1, a=0.28346E-05)

+ 0.00000 mol Al
( 1200.00 C, 1.0000 atm, S1, a=0.17649E-05) T

+ 0.00000 mol (NiO) (Al2O3)
( 1200.00 C, 1.0000 atm, S1, a=0.96457E-06)

+ 0.00000 mol NiO

```

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(1200.00 C, 1.0000 atm, S3, a=0.19745E-06)

Data on product species identified with "T" have been extrapolated
Data product species identified with "<---" or "<--s" have been drawn
from your private data collection

The third calculation below considers the ideal solution of the three oxides Al_2O_3 , Cr_2O_3 and NiO as well as the other solid phases. The solution phases which were not stable in the above calculation were not again considered. For brevity, the product list has been cut off at an activity of $10e^{-6}$.

The ideal solution of oxides has an activity identical to the Al_2O_3 phase listed below. This indicates that the energy of formation of NiO at this partial pressure of oxygen is not high enough to stabilize this oxide, if treated as an ideal solution. The excess energy, if sufficiently negative, would stabilize this oxide phase and result in NiO being present. Alternatively, an increase in the partial pressure would increase the energy of formation and again stabilize this oxide phase. Note that again that AlN has been calculated as a stable phase.

Output 3

DND/AIR VEHICLE RESEARCH SECTOR

0.89 Ni + 0.1 Cr + 0.01 Al +

.0079N2 + 0.0021 O2

=

0.43694E-02 mol	(1.0000	N2	
	+	0.25127E-07	Ni	<---
	+	0.25127E-07	Ni	
	+	0.20493E-07	Cr	<---
	+	0.20493E-07	Cr	
	+	0.23921E-10	Al	
	+	0.21881E-12	Al2O	
	+	0.19965E-12	CrO	
	+	0.80640E-13	NO	
	+	0.33238E-13	CrN	
	+	0.29984E-13	N	
	+	0.30607E-14	AlO	
	+	0.78542E-16	O	
	+	0.62924E-16	NiO	
	+	0.49552E-17	N2O	
	+	0.19897E-17	CrO2	
	+	0.18672E-17	N3	
	+	0.79808E-18	(AlO)2	
	+	0.66532E-19	AlN	
	+	0.72750E-20	Al2	
	+	0.79850E-21	O2	
	+	0.10305E-22	AlO2	
	+	0.27743E-25	NO2	
	+	0.12188E-25	CrO3)	
		(1200.00 C, 1.0000	atm, gas_ideal)	
+ 0.99014	mol	(0.89886	Ni	<--s

Annex C

```

+ 0.10100          Cr          <---s
+ 0.14022E-03      Al          <---s)
( 1200.00 C, 1.0000      atm, fcc)

+ 0.14000E-02 mol  ( 0.99995          Al2O3
+ 0.46491E-04      Cr2O3)
( 1200.00 C, 1.0000      atm, Corundum)

+ 0.00000          mol  ( 0.99991          Al2O3      :ideal solution, note activity is
+ 0.19745E-06      NiO          the same as the activity
+ 0.78050E-07      Cr2O3)      for Al2O3 below
( 1200.00 C, 1.0000      atm, solid, a=0.99991      )

+ 0.70613E-02 mol  AlN
( 1200.00 C, 1.0000      atm, S1, a= 1.0000      )

+ 0.00000          mol  Al2O3
( 1200.00 C, 1.0000      atm, S4, a=0.99991      )

+ 0.00000          mol  Ni
( 1200.00 C, 1.0000      atm, S1, a=0.89611      )

+ 0.00000          mol  Al2O3
( 1200.00 C, 1.0000      atm, S2, a=0.62609      )

+ 0.00000          mol  Al2O3
( 1200.00 C, 1.0000      atm, S3, a=0.58252      )

+ 0.00000          mol  Al2O3
( 1200.00 C, 1.0000      atm, S1, a=0.41511      )

+ 0.00000          mol  Ni3Al          <---
( 1200.00 C, 1.0000      atm, S1, a=0.21022      )

+ 0.00000          mol  CrN
( 1200.00 C, 1.0000      atm, S1, a=0.16055      )

+ 0.00000          mol  Cr
( 1200.00 C, 1.0000      atm, S1, a=0.94148E-01)

+ 0.00000          mol  Ni3Al
( 1200.00 C, 1.0000      atm, S1, a=0.72144E-01)

+ 0.00000          mol  Cr2N
( 1200.00 C, 1.0000      atm, S1, a=0.51077E-01)

+ 0.00000          mol  NiAl
( 1200.00 C, 1.0000      atm, S1, a=0.69770E-02)

+ 0.00000          mol  Al          T
( 1200.00 C, 1.0000      atm, S1, a=0.17649E-05)

```

Data on product species identified with "T" have been extrapolated
 Data product species identified with "<---" or "<---s" have been drawn
 from your private data collection

In the next calculation, the amount of air has increased by an order of magnitude. For brevity, the product list has been cut off at an activity of $10e^{-6}$. As expected, AlN does not

Annex C

appear and the ideal solution of oxides is now more stable than the corundum solution. As more oxygen is present, the oxide is now rich in Cr_2O_3 . The actual energy difference between the two oxide phases is only 450 Joules. Considering that NiO and Al_2O_3 form a spinel structure, the excess energy of mixing would likely be negative and this would further stabilize the NiO in the oxide.

Output 4

DND/AIR VEHICLE RESEARCH SECTOR

0.89 Ni + 0.1 Cr + 0.01 Al +

.079N2 + 0.021 O2

=

```

0.79000E-01 mol  (  1.0000      N2
                   + 0.25628E-07  Ni
                   + 0.16906E-07  Cr
                   + 0.37813E-10  CrO
                   + 0.18514E-10  NO
                   + 0.86519E-13  CrO2
                   + 0.29984E-13  N
                   + 0.27420E-13  CrN
                   + 0.18033E-13  O
                   + 0.14735E-13  NiO
                   + 0.41095E-14  Al
                   + 0.11377E-14  N2O
                   + 0.12072E-15  AlO
                   + 0.42090E-16  O2
                   + 0.18672E-17  N3
                   + 0.14826E-17  Al2O
                   + 0.12168E-18  CrO3
                   + 0.14624E-20  NO2
                   + 0.12415E-20  (AlO)2
                   + 0.93314E-22  AlO2
                   + 0.11430E-22  AlN
                   + 0.21471E-27  Al2)
                   ( 1200.00 C, 1.0000      atm, gas_ideal)

+ 0.00000      mol  ( 0.74266      Cr2O3  :now rich in Cr2O3
                   + 0.22095      Al2O3)
                   ( 1200.00 C, 1.0000      atm, Corundum, a=0.96361      )

+ 0.97200      mol  ( 0.91564      Ni
                   + 0.84363E-01  Cr
                   + 0.26559E-07  Al
                   ( 1200.00 C, 1.0000      atm, fcc)
                   <---s
                   <---s
                   <---s)

+ 0.14000E-01 mol  ( 0.64282      Cr2O3
                   + 0.35713      Al2O3
                   + 0.46238E-04  NiO)
                   ( 1200.00 C, 1.0000      atm, solid)

+ 0.00000      mol  Ni
                   ( 1200.00 C, 1.0000      atm, S1, a=0.91401      )

+ 0.00000      mol  Cr2O3
                   ( 1200.00 C, 1.0000      atm, S1, a=0.64282      )

+ 0.00000      mol  Al2O3
                   ( 1200.00 C, 1.0000      atm, S4, a=0.35713      )

```

Annex C

```

+ 0.00000      mol  Al2O3
  ( 1200.00 C, 1.0000      atm, S2, a=0.22362      )

+ 0.00000      mol  Al2O3
  ( 1200.00 C, 1.0000      atm, S3, a=0.20806      )

+ 0.00000      mol  Al2O3
  ( 1200.00 C, 1.0000      atm, S1, a=0.14826      )

+ 0.00000      mol  CrN
  ( 1200.00 C, 1.0000      atm, S1, a=0.13244      )

+ 0.00000      mol  Cr
  ( 1200.00 C, 1.0000      atm, S1, a=0.77668E-01)

+ 0.00000      mol  Cr3O4
  ( 1200.00 C, 1.0000      atm, S1, a=0.55182E-01)

+ 0.00000      mol  Cr2N
  ( 1200.00 C, 1.0000      atm, S1, a=0.34760E-01)

+ 0.00000      mol  AlN
  ( 1200.00 C, 1.0000      atm, S1, a=0.17179E-03)

+ 0.00000      mol  (NiO)(Al2O3)
  ( 1200.00 C, 1.0000      atm, S1, a=0.80675E-04)

+ 0.00000      mol  (NiO)(Cr2O3)
  ( 1200.00 C, 1.0000      atm, S1, a=0.80641E-04)

+ 0.00000      mol  CrO2
  ( 1200.00 C, 1.0000      atm, S1, a=0.51296E-04)      T

+ 0.00000      mol  NiO
  ( 1200.00 C, 1.0000      atm, S3, a=0.46238E-04)

+ 0.00000      mol  Ni3Al
  ( 1200.00 C, 1.0000      atm, S1, a=0.13151E-04)

+ 0.00000      mol  NiO
  ( 1200.00 C, 1.0000      atm, S2, a=0.49806E-05)      T

+ 0.00000      mol  NiO
  ( 1200.00 C, 1.0000      atm, S1, a=0.36067E-05)      T

+ 0.00000      mol  NiAl
  ( 1200.00 C, 1.0000      atm, S1, a=0.12225E-05)

```

Data on product species identified with "T" have been extrapolated
 Data product species identified with "<---" or "<--s" have been drawn
 from your private data collection

Under similar conditions, the oxide on a nickel 10at%Cr, 2 at% Al alloy at 1100°C in 0.1 atm of O₂ has been reported in literature as a mixture of Al₂O₃ and NiO/Al₂O₃/Cr₂O₃ oxide phases.¹ Adjusting the alloy and temperature, the results are given below. The addition of aluminum in the alloy has changed the major constituent in the oxides from Cr₂O₃ to Al₂O₃ and the NiO concentration in the ideal oxide solution has decreased. Yet overall, the energy

Annex C

separating the two oxide phases has increased to 600 Joules. These calculations are then in moderate agreement with observations given that the excess energy is not available and kinetic factors, such as ternary diffusion phenomena, have not been considered.

Output 5

DND/AIR VEHICLE RESEARCH SECTOR

0.88 Ni + 0.1 Cr + 0.02 Al +

.079N2 + 0.021 O2

=

```

0.79000E-01 mol ( 1.0000      N2
                  + 0.20575E-08 Ni
                  + 0.17868E-08 Cr
                  + 0.11641E-11 CrO
                  + 0.85834E-12 NO
                  + 0.17463E-14 N
                  + 0.16117E-14 CrN
                  + 0.10090E-14 CrO2
                  + 0.31634E-15 O
                  + 0.27336E-15 Al
                  + 0.19401E-15 NiO
                  + 0.54342E-16 N2O
                  + 0.30713E-17 AlO
                  + 0.26541E-18 O2
                  + 0.15316E-18 N3
                  + 0.62038E-19 Al2O
                  + 0.39768E-21 CrO3
                  + 0.17794E-22 (AlO)2
                  + 0.76007E-23 NO2
                  + 0.45133E-24 AlO2
                  + 0.24163E-24 AlN
                  + 0.26514E-29 Al2)
                  ( 1100.00 C, 1.0000      atm, gas_ideal)

+ 0.00000      mol ( 0.80697      Al2O3 :now rich in Al2O3
                  + 0.14175      Cr2O3)
                  ( 1100.00 C, 1.0000      atm, Corundum, a=0.94872      )

+ 0.97200      mol ( 0.90535      Ni      <--s
                  + 0.94650E-01 Cr      <--s
                  + 0.15147E-07 Al      <--s)
                  ( 1100.00 C, 1.0000      atm, fcc)

+ 0.14000E-01 mol ( 0.71428      Al2O3 :now rich in Al2O3
                  + 0.28571      Cr2O3
                  + 0.14431E-04 NiO)
                  ( 1100.00 C, 1.0000      atm, solid)

                  + 0.00000      mol Ni
                  ( 1100.00 C, 1.0000      atm, S1, a=0.89951      )

                  + 0.00000      mol Al2O3
                  ( 1100.00 C, 1.0000      atm, S4, a=0.71428      )

                  + 0.00000      mol Al2O3
                  ( 1100.00 C, 1.0000      atm, S2, a=0.41404      )

                  + 0.00000      mol Al2O3
                  ( 1100.00 C, 1.0000      atm, S3, a=0.37814      )

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Annex C

```

+ 0.00000      mol  Cr2O3
  ( 1100.00 C, 1.0000      atm, S1, a=0.28571      )

+ 0.00000      mol  CrN
  ( 1100.00 C, 1.0000      atm, S1, a=0.28117      )

+ 0.00000      mol  Al2O3
  ( 1100.00 C, 1.0000      atm, S1, a=0.25581      )

+ 0.00000      mol  Cr
  ( 1100.00 C, 1.0000      atm, S1, a=0.85381E-01)

+ 0.00000      mol  Cr2N
  ( 1100.00 C, 1.0000      atm, S1, a=0.83119E-01)

+ 0.00000      mol  Cr3O4
  ( 1100.00 C, 1.0000      atm, S1, a=0.12127E-01)

+ 0.00000      mol  AlN
  ( 1100.00 C, 1.0000      atm, S1, a=0.50728E-03)

+ 0.00000      mol  (NiO) (Al2O3)
  ( 1100.00 C, 1.0000      atm, S1, a=0.52429E-04)

+ 0.00000      mol  Ni3Al
  ( 1100.00 C, 1.0000      atm, S1, a=0.14800E-04)

+ 0.00000      mol  NiO
  ( 1100.00 C, 1.0000      atm, S3, a=0.14431E-04)

+ 0.00000      mol  (NiO) (Cr2O3)
  ( 1100.00 C, 1.0000      atm, S1, a=0.12000E-04)

+ 0.00000      mol  CrO2
  ( 1100.00 C, 1.0000      atm, S1, a=0.86380E-05)      T

+ 0.00000      mol  NiO
  ( 1100.00 C, 1.0000      atm, S2, a=0.20569E-05)      T

+ 0.00000      mol  NiO
  ( 1100.00 C, 1.0000      atm, S1, a=0.15102E-05)      T

+ 0.00000      mol  NiAl
  ( 1100.00 C, 1.0000      atm, S1, a=0.11432E-05)

```

Data on product species identified with "T" have been extrapolated
 Data product species identified with "<---" or "<--s" have been drawn
 from your private data collection

Reference

1. J.E. Morral, M.S. Thompson, O.F. Devereux, "Protective Scale Formation on Complex Alloys", in N.L. Peterson Memorial Symposium on "Oxidation of Metals and Associated Mass Transport, The Metallurgical Society, (Warren Pennsylvania) 1986, pp.315-321.

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The Ni-Al-Cr system is of importance to the gas turbine industry as it forms the basis for protective coating design and application for hot section components. These thermodynamic models establish a foundation upon which the metallurgical chemistry of aluminum coating processes for nickel base superalloys can be addressed. The thermodynamic model of the ternary system is based on the binary phase diagrams for each pair of components. Given the technological importance of this system, the robustness of the models developed for each of the binary systems will have a direct impact on the success of future engineering work. It is primarily for this reason that these binary systems are examined in detail. This technical memo reviews the thermodynamic concepts upon which phase diagram models are based and presents an effective model for each of the binary systems: Al-Cr, Al-Ni, and Ni-Cr.

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